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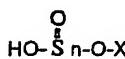
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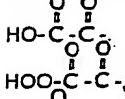
A request for correction of page 1 and claim 10 has been filed pursuant to Rule 88 EPC. A decision on the request will be taken during the proceedings before the Examining Division (Guidelines for Examination in the EPO, A-V, 2.2).

(54) Stannic acid anhydride.

(57) The invention provides stannic acid anhydride of formula:



wherein X represents



or HC-O- . It also provides conductive tin oxide products by baking the water-soluble reaction product of tin carboxylate and peroxide (e.g. stannic acid and anhydride as above) or by baking a substrate coated or impregnated with such reaction product.

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Description**STANNIC ACID ANHYDRIDE**

The present invention relates to stannic acid anhydrides suitable for forming transparent conductive tin oxide, and to conductive products comprising such tin oxide, and to their formation.

In recent years, with the remarkable development in the field of electro-optical elements, attention has been paid to transparent conductive films of SnO_2 or In_2O_3 . These have been developed, for example, as transparent electrodes of various optical devices such as those of electro-luminescent, liquid crystal and image accumulation devices, etc.; as heating elements or resistors utilizing their heat resistance and anti-abrasion properties; as solar cells utilizing their high conductivity; or as selective permeable films for use in solar heat electricity generation utilizing their high reflexivity in the infrared.

Known methods of forming these transparent conductive films are :

- (1) chemical vapor deposition ;
- (2) vacuum evaporation ;
- (3) sputtering ;
- (4) coating.

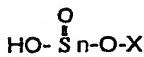
There is also a strong demand for conductive powder to give conductivity to paints, plastics, fibers, etc., and in Japanese Patent Kokai (Laid-open) No.77623/1986, a method is proposed in which titanium oxide-tin oxide type composite conductive powder is produced by mixing prescribed quantities of stannous oxalate and antimony chloride with titanium oxide and baking the mixture.

All of the above-mentioned methods (1)-(3) use complicated apparatus and are inferior in operability. In addition, they usually necessitate an etching step after film formation, to form a pattern.

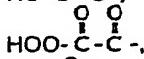
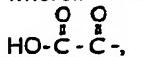
In method (4), when using an inorganic salt such as SnCl_4 for example, hydrogen chloride or other chloride gases are generated upon heat decomposition and severe corrosion of the apparatus takes place. Also, the chlorine remaining in the film may impair the conductivity. There are also methods using organic acid salts such as octyl acid tin salt or an organic complex, but these methods have problems -e.g. the uniformity of the film is impaired upon heat decomposition or gelation of the coating liquid takes place; moreover, they have defects such that the formed film is uneven, cloudy and is liable to damage.

By the method of the above-mentioned Japanese Patent Kokai, it is impossible to cover the surface of the titanium oxide with tin oxide, so that the conductivity is insufficient and the performance shows great fluctuation.

The present invention provides stannic acid anhydrides of formula:



wherein X represents



or $\text{HC}(=\text{O})-\text{O}-$, and conductive products covered with tin oxide obtainable by baking a substrate coated or impregnated with a water-soluble reaction product obtainable from tin carboxylate and peroxide (a reaction product such as the above-mentioned stannic acid anhydride) - instead, the dry reaction product can be baked as it is, without such coating or impregnation.

As the carboxylates used in the present invention may be mentioned for example, stannous formate, stannous acetate, stannous oxalate, stannous tartrate, etc.

Stannous oxalate is preferred.

As the peroxide, any may be used which can form a transparent aqueous solution of a tin compound by reacting with the tin carboxylate. For example there may be mentioned H_2O_2 ; alkali metal peroxides such as Li_2O_2 , Na_2O_2 , K_2O_2 , Rb_2O_2 , Cs_2O_2 , etc.; salts of alkali-metals or ammonium of peroxyoacids such as HNO_4 , H_3PO_5 , $\text{H}_4\text{P}_2\text{O}_8$, H_2SO_5 , $\text{H}_2\text{S}_2\text{O}_8$, etc.; hydroperoxides such as t-butylhydroperoxide, dimethylbenzylhydroperoxide, etc.; peroxides such as di(3-carboxypropanoyl)peroxide, sec-butanoyl-t-butylperoxide, acetyl t-butylperoxide, etc. Incidentally, when using alkali metal peroxides or salts of peroxyoacids, remaining alkali metal may impair the conductivity, so that H_2O_2 and organic peroxides such as hydroperoxides and peroxides are preferred.

There is no restriction as to the quantity of peroxide provided that it forms a transparent aqueous solution of the tin compound by reacting with a tin carboxylate. For example, when using H_2O_2 as the peroxide and the quantity is set at more than 1.5 mol, preferably in the range of 1.6 to 2.2 mol, for 1 mol of said tin salt, it is possible to further elevate the uniformity and conductivity of the finally obtained tin oxide coat.

As the aqueous medium, water is usually used, but an amount of water-miscible organic solvent may be used as well in a range in which viscosity rise or gelation of the reaction-produced solution does not occur.

A method of producing the aqueous solution is to add tin carboxylate to an aqueous medium with stirring, and then add a prescribed quantity of hydrogen peroxide.

For increased conductivity, the tin oxide product is preferably doped. Thus dopant may coexist in the reaction system, e.g. in the ratio of 0.01 to 0.6 mol, preferably 0.03 to 0.5 mol, for one mol of the tin carboxylate. Among such dopants may be mentioned compounds containing elements of Ib Group such as Cu, Ag, Au; those of IIb Group such as Cd; those of IIIa Group such as Ce, Eu; those of Va Group such as V, Nb, Ta; those of Vb Group such as As, Sb, Bi; those of VIa Group such as Cr, Mo, W; those of VIIa Group such as Re; those of VIII Group such as Ru, Rh, Pd, Os, Ir, Pt and fluorine. Compounds containing elements selected from Ib, Va, Vb, VIa, VIII Groups and fluorine are preferable. Presence of antimony oxides such as Sb_2O_3 , Sb_2O_4 , Sb_6O_{13} etc. or fluorine compounds such as SnF_2 , NH_4F in the reaction system makes it possible to form a uniform reaction-produced transparent aqueous solution and to provide tin oxide having very good conductivity, and so is especially desirable.

Even if the reaction is initiated at room temperature, there are cases where boiling may take place due to reaction heat. Therefore, when the reaction is conducted at a temperature below the boiling point, it is desirable that the concentration of the tin carboxylate should be generally below 20 weight %, preferably below 18 weight %.

In this way, a transparent aqueous solution of the tin compound can be obtained in a reaction time usually from 5 to 50 minutes. The aqueous solution without any treatment, or after suitable concentration, is baked to produce conductive tin oxide; or the solution is coated on or impregnated into the surface of a substrate and is baked to produce a conductive product covered with tin oxide.

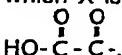
The baking conditions employed are generally temperatures from $400^{\circ}C$ to $1000^{\circ}C$, preferably from $500^{\circ}C$ to $800^{\circ}C$, for 0.5 to 5 hours, preferably for 1 to 3 hours.

Any substrate can be used which can withstand the conditions of baking.

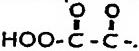
Such substrates include for example oxides such as zinc white, titanium oxide, antimony white, black iron oxide, red iron oxide, red lead, chromium oxide; sulfides such as lithopone, zinc sulfide, cadmium yellow; sulfates such as barium sulfate, gypsum, lead sulfate; carbonates such as barium carbonate, calcium carbonate powder, white lead; hydroxides such as alumina white; chromates such as chrome yellow, zinc yellow, barium chromate; metal powder such as zinc powder, aluminum powder; inorganic powder such as carbon black, glass beads, glass flake, mica, glaze; inorganic fibers such as carbon fiber, alumina fiber, glass fiber, rock wool, asbestos; ceramic shaped bodies such as tile, insulator, yarn guide; and inorganic products of any optional shape such as film, board, porous body, etc.

As regards the quantity of coating or impregnation, there is no restriction as long as conductive products covered with tin oxide can be obtained. For example, when the substrate is an inorganic powder, it is appropriate to regulate the coating or impregnation by the water-soluble reaction product so that the covering quantity of tin dioxide will be generally from 5 to 40% of the weight of the substrate.

When stannous oxalate as tin carboxylate and H_2O_2 as peroxide are reacted in a molar ratio of about 1 : 1 while regulating the temperature below about $50^{\circ}C$, preferably from 5 to $45^{\circ}C$ under cooling, it is possible to produce oxalic acid stannic acid anhydride which corresponds to the above-mentioned structural formula in which X is



In the same way as above except that the molar ratio of the two is 1 : 2, it is possible to produce monoperoxalic acid stannic acid anhydride of which X in the structural formula is



Also, by reacting stannous oxalate with H_2O_2 in a molar ratio of about 1 : 2 at a temperature above about $70^{\circ}C$, preferably between 80° and $100^{\circ}C$, it is possible to produce performic acid stannic acid anhydride, of which X in the structural formula is



For isolating oxalic or peroxalic acid stannic acid anhydride, freeze drying is recommended; drying for example above $70^{\circ}C$ by-produces a mixture of complicated compounds.

The novel stannic acid anhydride of the present invention makes it possible to form tin oxide of excellent transparency and conductivity, in any optional form such as powder, film or fiber form, without problems of using a complicated apparatus, or inferior operability.

Also, according to the present invention, by baking a substrate coated or impregnated with the water-soluble reaction product, a uniform tin oxide film is formed on the surface of the substrate, and thus a product of excellent conductivity is provided in an industrially advantageous manner, while the shape of the substrate is utilized as it is.

The resulting products are widely applicable not only in fillers, paints, additives for electrostatic recording paper, films, fibers, etc. in which conductivity and electromagnetic wave shielding properties are especially demanded, but also in transparent heating elements, gas sensors, infrared reflexing films, lithium ion selective adsorbing agents, catalysts, flame-retardants, etc.

The present invention is further illustrated by the following Examples.

The bulk density and the resistivity ($\Omega \cdot cm$) were obtained as follows: A sample of 10 g is packed into a cell

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(inner diameter: 20.5 mm; length: 50 mm); the compressed height h (mm) was measured by an electrode piston (inner diameter: 20 mm; length: 60 mm) under a load of 1 t/cm^2 , and the electric resistance R (Ω) was measured using a four-probe ohm meter (3224 type) produced by Hioki Denki Co. Ltd.

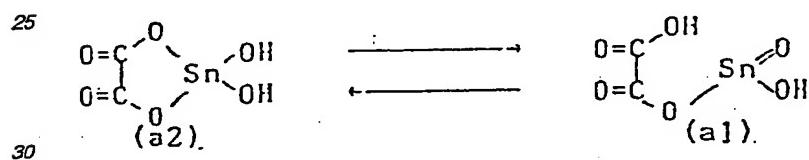
5 Example 1

190 g stannous oxalate (SnC_2O_4) was added to 1 liter water, and while the reaction temperature was regulated at a temperature below 40°C in an ice bath, 90 g aqueous 35 weight % H_2O_2 solution was added under stirring. The mixture was reacted for 30 minutes to produce a transparent aqueous solution (a) of oxalic acid stannic acid anhydride.

This transparent aqueous solution (a) showed a very low pH of 0.6 and showed a two stage dissociation by potentiometric titration. From this, it is apparent that there are two kinds of acid functional group in the molecule of the resulting product with one of them showing a strong acidity comparable to sulfuric acid, and the generation of oxalic acid stannic acid anhydride was confirmed.

Crystals obtained by freeze-drying the transparent aqueous solution (a) were soluble in both water and methanol.

About 0.3 ml of the transparent aqueous solution (a) diluted with about 0.3 ml heavy water was measured for ^{13}C -NMR. With TMS (tetramethylsilane) used as the external standard, a sharp single line was observed at 160.9 ppm, and the UV spectrum had absorption maxima in the vicinity of 230, 260 and 300 nm, which correspond to the absorption maximum values of tin oxalate, oxalic acid, and meta stannic acid. From this fact, it is considered that there exists an equilibrium condition due to intramolecular rearrangement between the product (a1) of the present invention and the compound (a2) of the following structure.



In the same way as above except that 0.1 mol Sb_2O_3 , for one mol of SnC_2O_4 was added together with SnC_2O_4 , a transparent aqueous solution (b) was obtained.

After spray-drying the transparent aqueous solutions (a and b), they were ground with a ball mill into powders having an average particle diameter of about 5μ . These powders were baked in the atmosphere at 500°C for 3 hours to produce two kinds of tin oxide powder (A and B).

The resistivity was obtained, and the results are shown in Table 1 below:

Table I

Sample name	Bulk density (g/ml)	Resistivity ($\Omega \cdot \text{cm}$)
A	2.4	3×10^2
B	2.4	7×10^{-1}

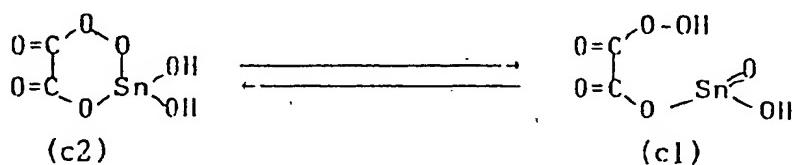
55 Example 2

To one liter water was added 210 g SnC_2O_4 . While regulating the reaction temperature below 40° in an ice bath, 200 g aqueous 35 weight % H_2O_2 solution was added under stirring, and the mixture was reacted for 30 minutes to obtain a transparent aqueous solution (c) of monoperoxalic acid stannic acid anhydride.

60 This transparent aqueous solution (c) had a very low pH of 0.8, and showed one stage dissociation by potentiometric titration. From this fact, it is apparent that the solution has a structure comparable to sulfuric acid.

About 0.3 ml of the transparent aqueous solution (c) diluted with about 0.3 ml heavy water was measured for $^{13}\text{C-NMR}$. With TMS (tetramethylsilane) used as the external standard, a single sharp line was observed at 161.4 ppm. From this, it is considered that there is an equilibrium condition due to intramolecular

rearrangement between the compound (c1) of the present invention and the compound (c2) of the following structure:



In the same way as above except that 0.1 mol Sb_2O_3 for one mol of SnC_2O_4 was added to the reaction system together with SnC_2O_4 , a transparent aqueous solution (d) was obtained.

After the transparent aqueous solutions (c and d) were spray-dried, they were ground with a ball mill into powders of an average particle diameter of about $5\text{ }\mu$, and the powders were baked in the atmosphere at 500° for 3 hours to produce two kinds of tin oxide powders (C and D).

The resistivity was measured, and the results are shown in Table 2 shown below:

Table 2

Sample name	Bulk density (g/ml)	Resistivity ($\Omega \cdot \text{cm}$)
C	2.6	2×10^2
D	2.6	5×10^{-1}

Example 3

Two hundred and ten g (210 g) SnC₂O₄ was added to one liter water, and 200 g aqueous 35 weight % H₂O₂ solution was added under stirring. The mixture was reacted at a temperature of from 95° to 97°C for 30 minutes to obtain a transparent aqueous solution (e) of performic acid stannic acid anhydride. During the reaction, generation of carbon dioxide was observed.

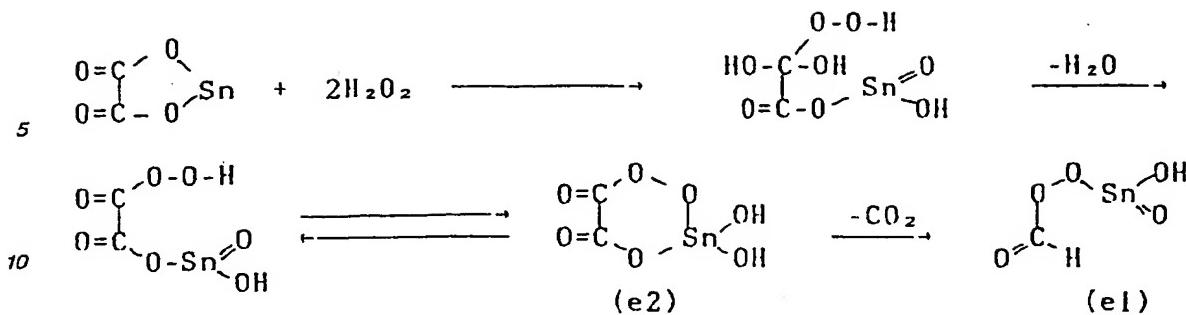
Since the transparent aqueous solution (e) showed a very low pH of 0.8 and showed one stage dissociation by potentiometric titration, it is apparent that the solution has a structure showing a strong acidity comparable to sulfuric acid.

The powder obtained by freeze-drying the transparent aqueous solution (e) was insoluble in water, and this is considered to have resulted from dehydration condensation which occurred during drying.

About 0.3 ml of the transparent aqueous solution (e) diluted with about 0.3 ml heavy water was measured for ^{13}C -NMR. With TMS (tetramethylsilane) used as the external standard, a relatively sharp signal and a swelling

From the above-mentioned results, it is considered that peroxylic acid stearic acid esterhydrate (1) is

From the above-mentioned results, it is considered that peroxalic acid stannic acid anhydride (e1) is generated by the following reaction mechanism, and the compound (e2) also coexists.



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In the same way as above except that 0.1 mol Sb₂O₃ for one mol of SnC₂O₄ was added together with SnC₂O₄, a transparent aqueous solution (f) was obtained.

20 After the transparent aqueous solutions (e and f) were spray-dried, they were ground with a ball mill into powders of an average particle diameter of about 5 μ and the powders were baked in the atmosphere at 500°C for 3 hours to produce two kinds of tin oxide powders (E and F).

The resistivity was measured, and the results are shown in the following Table 3.

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Table 3

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Sample name	Bulk density (g/ml)	Resistivity (Ω.cm)
E	3.4	5 × 10 ¹
F	3.4	7 × 10 ⁻²

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Example 4

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The transparent aqueous solution (f) of Example 3 was spinner-coated at 3000 rpm on a quartz glass substrate, and was baked in the atmosphere at 700°C for 2 hours to produce a transparent conductive film.

The properties of the film are shown in Table 4.

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Table 4

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Thickness (Å)	Percent transmission (%)	Resistivity * (Ω.cm)	Surface
300	90	6 × 10 ⁻²	Smooth, uniform

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* Resistivity was calculated from the electric resistance by four-probe method and the film thickness.

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Example 5

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SnC₂O₄ was added to room temperature water, and aqueous 35 weight % H₂O₂ solution was added under stirring in the ratio of 2 mols for one mol of SnC₂O₄, and the mixture was reacted for 30 minutes at a temperature of about 95°C generated by reaction heat, to produce a transparent aqueous solution (g) of the reaction product.

A transparent aqueous solution (h) was produced in the same way as above except that 0.1 mol Sb₂O₃ for one mol of SnC₂O₄ was added together with SnC₂O₄. In both cases, the concentration of SnC₂O₄ in the reaction system was set at 15 weight %.

To one weight part aliquots of the thus-produced transparent aqueous solutions (g and h), 4 weight parts of titanium oxide (TA-300, particle diameter 0.3 μ, produced by Fuji Titan Co.), glass beads (particle diameter 13 μ, produced by Toshiba Glass Co.), and mica (fin powder of white mica, particle diameter 1μ) were added respectively. Then, by drying, the water-soluble reaction products were fixed on the surface of substrates. Incidentally, adhesion between the powder particles of the substrate was not observed.

Then the substrates were baked in the atmosphere at 500°C for 3 hours to produce 6 samples to be tested.

The resistivity was measured, and the results are shown in Table 5.

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Table 5

Sample name	Kind of transparent aqueous solution	Kind of substrate	Resistivity (Ω.cm)
G1	g	Titanium oxide	7 × 10 ⁴
G2	g	Glass beads	7 × 10 ⁴
G3	g	Mica	9 × 10 ⁴
H1	h	Titanium oxide	4 × 10 ⁻¹
H2	h	Glass beads	4 × 10 ⁻¹
H3	h	Mica	3 × 10 ⁻¹

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From the above Table, it is clearly understood that the products of the present invention, especially those combined with dopant, have excellent conductivity.

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Example 6

Two samples for testing (H4 and H5) were produced in the same way as Example 5 H1 except that glass fiber (diameter 15 μ; length 3 mm) and asbestos (Canadian chrysotile No.1) were used as the substrates. The results are shown in Table 6.

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Table 6

Sample name	Kind of substrate	Resistivity (Ω.cm)
H4	Glass fiber	3 × 10 ⁻¹
H5	Asbestos	5 × 10 ⁻¹

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Example 7

A sample for testing (H6) was produced in the same way as Example 5 except that the transparent aqueous solution (h) was fixed by spraying onto a tile (unglazed tile, produced by Yodogawa Sangyo Co.).

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The surface resistance was measured by a surface resistance tester (MCP tester produced by Mitsubishi Petrochemical Co. Ltd.). The result was 500 Ω/cm².

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Example 8

A sample for testing (H7) was produced in the same way as Example 5 H1 except that t-butyl hydroperoxide was used instead of H_2O_2 and 0.4 mol NH_4F was used instead of Sb_2O_3 .

5 The sample showed an excellent conductivity, with the resistivity being $7 \times 10^{-1} \Omega.cm$.

Example 9

Transparent aqueous solutions (i and j) were produced in the same way as Example 5 except that 1.5 mol di(3-carboxy propanoyl) peroxide was used instead of 2 mol H_2O_2 and except that 0.3 mol NH_4F for one mol of 10 SnC_2O_4 was used, and in the same way as Example 3, tin oxide powders (I and J) were produced.

The resistivity was measured and the results are shown in Table 7.

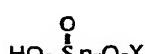
Table 7

Sample name	Resistivity ($\Omega.cm$)
I	7.4×10^1
J	8.9×10^{-2}

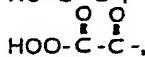
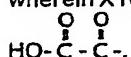
25 The present invention provides novel tin compounds which involve little or no apparatus restrictions or problems, are widely applicable, and can finally form tin oxide of excellent transparency and conductivity in an industrially advantageous manner. The invention can provide products having a uniform tin oxide film on a substrate of any form (such as powder form, film form, fiber form, etc.) to give excellent conductivity.

Claims

35 1. Stannic acid anhydride of formula :



wherein X represents



or $H-C\overset{O}{|}-O-$.

50 2. A conductive tin oxide product obtainable by baking an anhydride according to claim 1 or by baking a substrate coated or impregnated with anhydride according to claim 1.

3. A conductive tin oxide product obtainable by baking a water-soluble product obtainable by reaction of tin carboxylate with peroxide.

4. A conductive tin oxide product obtainable by baking a substrate coated or impregnated with water-soluble product obtainable by reaction of tin carboxylate with peroxide.

5. A conductive tin oxide product according to claim 2 or 3 or 4 wherein the tin oxide incorporates dopant.

6. A method of forming a conductive tin oxide product which comprises reacting tin carboxylate with peroxide in an aqueous medium, drying the resulting reaction product solution, and baking the dried reaction product.

60 7. A method of making a conductive tin oxide product which comprises reacting tin carboxylate with peroxide in an aqueous medium, coating or impregnating a substrate with the resulting reaction product solution, and baking the coated or impregnated substrate.

8. A method of making a conductive tin oxide product which comprises forming a solution of compound according to claim 1 in an aqueous medium, and then (a) drying the solution and baking the dried product



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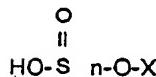
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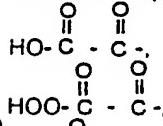
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European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 88 30 7247

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X, P	EP-A-0 235 968 (JAPAN EXLAN) * claims 1,3,4 * ---	1,6,10	C 07 F 7/22 C 03 C 17/25 C 09 D 5/24 H 01 B 1/08
X	SU-A- 541 849 (T.F. DOBROCHOTOVA et al.) * claims; column 1, line 19, example 1; column 5, lines 26-34 * ---	1,6,10	
A	US-A-3 853 612 (L. SPANOUDIS) * column 3 * ---	6	
A	CHEMICAL ABSTRACTS vol. 105, no. 20, 17 November 1986, abstract no. 175228u, Columbus, Ohio, US; & JP-A-6184380 (KOKAI TOKKYO KOHO) 28.04.1986 ----	6	
A	CHEMICAL ABSTRACTS vol. 99, no. 20, 14 November 1983, abstract no. 160791f, Columbus, Ohio, US; & SU-A-103683 (V.P. KARLOV et al.) 07.08.1983 -----	6	TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 07 F 7/22 C 03 C 17/25 C 09 D 5/24 H 01 B 1/08
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
BERLIN	11-07-1990	KAPTEYN H G	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
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or (b) coating or impregnating a substrate with the solution and baking the coated or impregnated substrate.

9. A method according to claim 6 or 7 or 8 wherein dopant for the tin oxide product is included in the aqueous medium.

10. A method of forming a compound according to claim 1 which comprises reacting tin oxylate with peroxide. 5

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